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ANTISTATIC AGENT FOR FIBRES

What is Claimed is:

1. An antistatic agent for fibres, characterised in that, the agent contains both nitrate(s) of calcium and/or magnesium (A) and lower amine salt and/or alkaline metal salt of lower carboxylic acid (B).

2. The antistatic agent according to claim 1, wherein the lower carboxylic acid is a carboxylic acid having 1 to 5 carbon(s).

3. The antistatic agent according to claim 1 or 2, wherein the lower amine salt is a salt with a monoamine (a) represented by the formula

$$N(.R^1)(.R^2)(.R^3) \qquad (1)$$

(in the formula, R^1 is a hydroxyalkyl group having 1 to 6 carbon(s), an alkyl group having 1 to 6 carbon(s), an alkenyl group or an aryl group; R^2 and R^3 each is hydrogen atom, a hydroxyalkyl group having 1 to 6 carbon(s), an alkyl group having 1 to 6 carbon(s), an alkenyl group having 1 to 6 carbon(s) or an aryl group; and R^1 and R^2 or R^1, R^2 and R^3 may be connected each other forming a five- to seven-membered ring together with N) and/or a salt with a polyamine substance (b) selected from the group consisting of a polyamine

represented by the formula

$$N(.R^6)(.R^7)\text{-}[\text{-}(CH_2)_nN(.R^8)\text{-}]_m\text{-}(CH_2)_nN(.R^4)(.R^5) \qquad (2)$$

(in the formula, R^4, R^5, R^6, R^7 and R^8 each is hydrogen atom or an alkyl group having 1 to 4 carbon(s); m is an integer of 0 to 4; n is an integer of 2 to 6; and, when m is 0, R^5 and R^7 or R^4, R^5 and R^7 may be connected each other to form a five- to seven-membered ring together with N-(-CH_2)$_n$-N) and a guanidine substance.

4. The antistatic agent according to any of claims 1 to 3, wherein the ratio of (A) to (B) is from 1:1 to 1:0.1 by weight.

Detailed Description of the Invention:

The present invention relates to an antistatic agent for fibre and, more particularly, it relates to an antistatic agent where an antistatic property to synthetic fibre, particularly polyester fibre, at low temperature is good and, even when a dyed product with a disperse dye is processed by that, the dyed product is not discolored.

Fibre, particularly synthetic fibre, is apt to be charged with static electricity and, during the course of finishing step, sewing step, etc. of fibre, troubles in operations are apt to happen. Such a disadvantage is particularly significant at low humidity such as 40% relative humidity or lower.

Nitrate of calcium or magnesium is used as an antistatic agent for fiber having an excellent antistatic property at low temperature (Japanese Laid-Open Patent No. 53/122,899). However, when it is adhered to a polyester fibre dyed with a disperse dye and subjected to a thermal treatment at the temperature of 160°C or higher, it sometimes happens that the disperse dye is degraded by nitrate ion and discoloration takes place. Especially in the case of dyed fibre using an anthraquinone dye as a disperse dye, discoloration upon thermal treatment may occur.

The present inventors have carried out extensive investigations for an antistatic agent having the above-mentioned problem and, as a result, they have achieved the present invention. Thus, the present invention relates to an antistatic agent for fibres, characterised in that, the agent contains both nitrate(s) of calcium and/or magnesium (A) and lower amine salt and/or

alkaline metal salt of lower carboxylic acid (B).

The nitrate(s) of calcium and/or magnesium (A) used in the present invention may be common one(s) and an example of nitrate of calcium is calcium nitrate tetrahydrate while an example of nitrate of magnesium is magnesium nitrate hexahydrate. Nitrates of calcium and magnesium may be used together.

In the lower amine salt and/or alkaline metal salt of the lower carboxylic acid (B) which are/is used in the present invention, examples of the lower carboxylic acid are carboxylic acids having 1 to 5 carbon(s). Specific examples thereof are monocarboxylic acids (such as formic acid, acetic acid, propionic acid, n-butyric acid and n-pentanoic acid) and dicarboxylic acid (such as oxalic acid and malonic acid) having 1 to 5 carbon(s). Among those, preferred ones are carboxylic acids having 1 to 3 carbon(s). In the case of carboxylic acid where carbons are more than 5, an effect of prevention of discoloration for the fibre dyed with disperse dye is little.

In the present invention, the lower amine in the lower amine salt is an amine which has no long-chain aliphatic hydrocarbon group of 7 or more carbon atoms. Examples of such an amine are a monoamine (a) represented by the formula

$$N(.R^1)(.R^2)(.R^3) \qquad (1)$$

(in the formula, R^1 is a hydroxyalkyl group having 1 to 6 carbon(s), an alkyl group having 1 to 6 carbon(s), an alkenyl group or an aryl group; R^2 and R^3 each is hydrogen atom, a hydroxyalkyl group having 1 to 6 carbon(s), an alkyl group having 1 to 6 carbon(s), an alkenyl group having 1 to 6 carbon(s) or an aryl group; and R^1 and R^2 or R^1, R^2 and R^3 may be connected each other forming a five- to seven-membered ring together with N) and/or a polyamine (b) selected from the group consisting of a polyamine represented by the formula

$$N(.R^6)(.R^7)\text{-}[\text{-}(CH_2)_nN(.R^8)\text{-}]_m\text{-}(CH_2)_nN(.R^4)(.R^5) \qquad (2)$$

(in the formula, R^4, R^5, R^6, R^7 and R^8 each is hydrogen atom or an alkyl group having 1 to 4 carbon(s); m is an integer of 0 to 4; n is an integer of 2 to 6; and, when m is 0, R^5 and R^7 or R^4, R^5 and R^7 may be connected each other to form a five- to seven-membered ring together with $N\text{-}(\text{-}CH_2)_n\text{-}N$) and a guanidine

substance.

Examples of the hydroxylakyl group having 1 to 6 carbon(s) for R^1, R^2 and R^3 in the formula (1) are hydroxyethyl group, hydroxyl-n- or isopropyl group, hydroxyl-n- or isobutyl group, hydroxypentyl group and hydroxyhexyl group. Examples of the alkyl group having 1 to 6 carbon(s) are methyl group, ethyl group, n- or isopropyl group, n- or isobutyl group, n-pentyl group and n-hexyl group. An example of the alkenyl group having 1 to 6 carbon(s) is propenyl group. Examples of the aryl group are phenyl group, naphthyl group, an alkaryl group where carbon numbers of the alkyl moiety are 6 or less (preferably, 4 or less) (such as tolyl group) and aralkyl group (such as benzyl group). In some cases, R^1 and R^2 may be connected each other forming a divalent organic group having 4 to 6 carbons such as $-(-CH_2-)_p$ (p is an integer of 4 to 6) or $-CH_2CH_2OCH_2CH_2-$ forming a five- to seven-membered ring such as $-N\begin{pmatrix}\frown\\ \smile\end{pmatrix}(CH_2)_p$ or $-N<\begin{matrix}CH_2CH_2\\ CH_2CH_2\end{matrix}>O$. In some cases, R^1, R^2 and R^3 may be connected each other together with N forming a five- to seven-membered ring such as $\begin{matrix}CH & = & CH\\ | & & |\\ N=CH & CH & =CH\end{matrix}$.

When carbon numbers of the alkyl group, the alkenyl group or the hydroxylalkyl group in R^1, R^2 and R^3 are more than 6, an effect of preventing the discoloration of dyed fibre with disperse dye is little.

Examples of the alkyl group having 1 to 4 carbon(s) for R^4 to R^8 in the formula (2) are methyl group, ethyl group, n- or isopropyl group and n- or isobutyl group.

m is an integer of 0 to 4 and n is an integer of 2 to 6. When m is 0, R^5 and R^7 may be connected each other together with $N-(-CH_2)_n-N$) to form a five- to seven-membered ring such as $-N<\begin{matrix}CH_2CH_2\\ CH_2CH_2\end{matrix}>N-$ or R^4, R^5 and R^7 may be connected each other together with $N-(-CH_2)_n-N$) to form a five- to seven-membered ring such as $-N<\begin{matrix}CH=N\\ |\\ CH_2CH_2\end{matrix}$.

④ Alicyclic amine salt or heterocyclic amine salt of lower carboxylic acid:

Morpholine propionate, etc.

(2) Polyamine salt of lower carboxylic acid

① Polyalkylenepolyamine salt of lower carboxylic acid:

Diethylenetriamine acetate, triethylenetetramine formate, dimethylaminopropylamine acetate, etc.

② Heterocyclic polyamine salt of lower carboxylic acid:

Imidazole formate, etc.

③ Guanidine salt of lower carboxylic acid:

Guanidine acetate, etc.

[2] Alkaline metal salt of lower carboxylic acid

Potassium formate, sodium acetate, potassium propionate, potassium n-butyrate, sodium n-pentanoate, etc.

When salt is a lower amine salt in the case of a salt (B) of lower carboxylic acid, the ratio of the lower carboxylic acid to the lower amine used for the formation of the salt is usually from 1:0.5 to 1:1.5 or, preferably, from 1:0.9 to 1:1 in terms of ratio by equivalent. When the salt is an alkaline metal salt, the ratio of the lower carboxylic acid to the alkaline metal hydroxide used for the formation of the salt is usually from 1:0.5 to 1:1.1 or, preferably, from 1:0.9 to 1:1 in terms of ratio by equivalent. When the lower amine or the alkaline metal hydroxide is less than 0.5, an effect of preventing the discoloration of dyed fibre with disperse dye lowers. When the lower amine is more than 1.5 or the alkaline metal hydroxide is more than 1.1, precipitate of calcium hydroxide or magnesium hydroxide is formed and stability of the solution is deteriorated.

The antistatic agent of the present invention contains both nitrate(s) of calcium and/or magnesium (A) and lower amine and/or alkaline metal salt(s) (B) of lower carboxylic acid. The compounding ratio of (A) to (B) may vary depending upon the compounds used and, usually, it is from 1:1 to 1:0.1 or, preferably, from 1:0.6 to 1:0.3 by weight. When (B) is more than 1 in the above-mentioned usual compounding ratio, the antistatic effect is deteriorated while, when (B) is less than 0.1, an effect of preventing the discoloration of dyed fibre with disperse dye becomes poor.

The antistatic agent of the present invention is used for fibre and example of the fibre or fibrous textile to be applied are synthetic fibres such as polyester, polyamide (Nylon), polyester ether, polyacrylate (e.g., polyacrylonitrile), polyvinyl chloride and polyolefin (e.g., polypropylene); semi-synthetic fibres

such as triacetate and diacetate; mixed materials thereof with natural fibres such as wool, cotton and silk; and inorganic fibres such as glass fibre. Examples of the fibrous textile are yarn, fabric, knitted product, nonwoven fabric, felt and carpet.

Amount of the antistatic agent applied may vary depending upon the antistatic degree, shape of the fibrous textile to be treated and type of the fibre constituting the same and, usually, the amount as a solid is 0.01 to 5% or, preferably, 0.1 to 2% to the weight of the fibre. When the applied amount is less than 0.01%, the effect in view of antistatic property is insufficient while, when it is more than 5%, texture of the treated fibre textile may become coarse.

The antistatic agent is applied to fibre after making into a treating solution or a treating bath (substituted with a treating solution) and, with regard to a method for the preparation of the treating solution, it is possible to use any of methods such as a method where a concentrated aqueous solution, aqueous dispersion or a solution in other appropriate solvent of each compound is mixed and the resulting concentrated antistatic agent solution is used after diluting to an appropriate concentration for applying to fibre and a method where each of the compounds is prepared and, in actual use, a treating solution for fibre in an appropriate concentration is directly prepared from them whereupon it is subjected to the treatment of fibre as a treating solution containing the antistatic agent of the present invention.

Examples of other appropriate solvent are lower aliphatic alcohols such as methanol and ethanol; polyhydric alcohols such as glycerol and triethylene glycol; alcohols having ether bond such as methyl carbitol and ethyl carbitol; ketones such as acetone and methyl ethyl ketone; other polar solvents such as dimethyl sulphoxide and dimethylformamide; and a mixture of two or more of the above-mentioned ones. Concentration of the effective solid of the antistatic agent in the treating solution may vary depending upon a method for application of the treating solution and to a type of the fiber or the fibrous textile and, usually, it is from 0.01 to 5% by weight or, preferably, from 0.05 to 2% by weight.

Examples of a method for applying the treating solution to fiber or fibrous textile are common methods such as a padding method, a spraying method and a dipping method.

Application of the agent is often carried out to the fibre or the fibrous textile after being subjected to a coloring treatment such as textile printing.

Temperature of the treating solution may be usually ambient temperature. After the fibre is treated with the treating solution, it is usually dried at 40 to 130°C for 30 to 1 minute(s) and then subjected to a thermal treatment at 150 to 200°C for 3 minutes to 30 seconds.

The antistatic agent of the present invention does not discolor the dyed fibre especially when applied to polyester fibre of fibrous textile dyed with a disperse dye. Usually, the disperse dye is a nonionic dye where the disperse dye *per se* is insoluble in water and the dye *per se* does not exhibit ionic property. Examples of the disperse dye are azo dyes, anthraquinone dyes, nitrodiphenylamine dyes, naphthalimide dyes, naphthoquinoneimide dyes and methine dyes. The case where discoloration is a problem is a fibre dyed with a disperse dye of an anthraquinone type. Examples of the disperse dye of an anthraquinone type are listed in pages 748 to 792 of "Shinpan Senryo Binran (New Handbook of Dyes)" edited by the Society of Organic Synthetic Chemistry; published by Maruzen. Specific examples are C. I. Disperse Yellow 51, C. I. Disperse Orange 11, C. I. Disperse Red 4, 9, 11, 15, 53, 55, 59, 60, 91, 92, 100, 104, 116 and 127, C. I. Disperse Violet 1, 4, 6, 8, 18, 23, 26.28, 30 and 37, C. I. Disperse Blue 1, 3, 5, 7, 14, 19, 26, 27, 52, 54, 55, 56, 60, 61, 62, 64, 72, 73, 81, 87, 90, 91, 97, 98, 99, 103, 104 and 105 and C. I. Disperse Green 1.

In a finishing process for fibrous products, there are simultaneously used processing agents such as paste, resin, softener, smoothening agent, water repellent, oil repellent, water-absorption processing agent, anti-staining processing agent, friction enhancer, flame retardant, glossing agent, delustrant and colour fastness enhancer in addition to an antistatic agent for giving texture and other characteristics. The antistatic agent of the present invention does not disturb the joint use with them and, depending upon the object, any of the processing agents may be used together.

Discoloration of dyes which has been a problem does not occur when the antistatic agent of the present invention is used especially to polyester fibre dyed with a disperse dye particularly that of an anthraquinone type. Thus, the antistatic agent of the present invention is a dye causing no such a problem. In addition, the fibre or fibrous textile which is treated with the antistatic agent of the present invention shows an excellent property of

Table 2

No.	Anti-discoloration	Electric Resistance (Ω)	Friction Zone Voltage (V)
A	o	6×10^9	120
B	o	7×10^9	250
C	Δ	2×10^9	45
D	o	1×10^9	50
E	o	2×10^9	55
F	o~Δ	8×10^9	290
G	o	4×10^9	110
H	o	2×10^9	40
I	o	5×10^9	105
J	o	7×10^9	130
K	o	6×10^9	120
L	×	9×10^9	25
M	×	4×10^9	85
–	o	$\geq 10^{12}$	2800

–: no antistatic agent

Example 2

Polyester-processed yarn textile dyed with 0.05% o.w.f of the disperse dye shown in Table 3 was dipped in a bath containing 10 g of the antistatic agent (A) prepared in Example 1, 20 g of Safanol E-04 (a cationic softener manufactured by Sanyo Chemical Industry) and 970 g of water and the same treatment as in Example 1 was carried out. The case where the antistatic agent (L) used and the case where no antistatic agent was not used were also subjected to the same treatment as in the case of the antistatic agent (A). The result is shown in Table 3. It is understood that the antistatic agent (A) of the present invention show good antistatic property and anti-discloration property. Further, all of the textures were nearly in the same degree and the effect of the softener was not lost.

Table 4

	Treated Cloth D (according to the present invention)	Treated Cloth L	Treated Cloth O
Electric Resistance (Ω)	8×10^9	6×10^9	$\geq 10^{12}$
Friction Zone Voltage (V)	200	150	4,200
Anti-Discoloration Property	o	×	o

[End]